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Synthesis and Characterization of Zinc Oxide Nanoparticles by a solution-free mechanochemical Reaction

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Abstract- **Zinc oxide plays an important role in current industry due to its special characteristics such as anti-corrosion, anti-bacteria, has low electrons conductivity and excellent heat resistance. Therefore the objectives of this study, pure zinc oxide nanoparticles (ZnO) were successfully synthesized by a solution-free mechanochemical reaction using zinc acetate dihydrate and oxalic acid as the precursor. The as-prepared precursor was calcined at 500°C temperatures for 2h to form ZnO nanoparticles. The phase and structural transformations were investigated by X-ray diffraction (XRD) and Fourier Transform Infrared Spectroscopy (FT-IR). FT-IR spectra of ZnO nanoparticles showed peaks in the region between 538 and 486cm-1 which corresponds to the stretching vibration of Zn – O band. The XRD studies showed a rather more crystalline behaviour of the nanoparticles and the grain size was calculated using Scherer's formula and found to be 18nm. XRD spectra revealed that the ZnO crystal has a hexagonal wurtzite structure and the strongest three diffraction peaks at 2θ=31.88°, 34.61° and 36.29° which are in close agreement to the literature. Scanning electron microscopy (SEM) has been used to study the morphological features of the ZnO nanopowder. Result of EDAX (Energy Dispersive X-Ray Spectroscopy) characterization shows that the ZnO nanoparticles has good purity (Zinc content of 49.84% and Oxygen content of 50.16%). The corrosion inhibition efficiency of the nanoparticles were calculated for mild steel in 0.1M HCl and 3.5% NaCl solution using Electrochemical Impedance Spectroscopy (EIS) and Polarization (Tafel) studies.**

Keywords: - ZnO, Nanostructure, Mechanochemical Synthesis, Morphological Effect, Electrochemical studies.

I. INTRODUCTION

Nanotechnology can be understood as a technology of design, fabrication and applications of nanostructures and nanomaterials, as well as fundamental understanding of physical properties and phenomena of nanomaterials and nanostructures [1]. Metal oxides nanostructures play crucial role in many areas of chemistry, physics and materials science [2]. The different properties of oxides enable the numerous applications in the fabrication of microelectronic circuits, sensors, piezoelectric devices, fuel cells, coatings against corrosion and as catalysts (most catalysts involve an oxide as active phase).
ZnO is an important metal oxides that could be easily grown, environmental friendly and of interest to many applications. It is suitable for industrial, technical and medical applications due to its diverse properties which have been found to strongly depend on their morphology [3] and thus has been the subject of study by many researchers. Various methods have been reported for the synthesis of ZnO nanoparticles, including precipitation, hydrothermal, sol-gel, thermal evaporation and mechanochemical methods. The mechanochemical method is one of the most frequently utilized methods for the synthesis of ZnO nanoparticles due to its excellent advantages such as low cost, low temperature, non-toxic operation and environmental friendliness. Since such reactions do not involve organic solvents, therefore for controlling the nucleation and growth of nanoparticles, they are attractive from an environmental point of view.
Zinc oxide nanoparticles have been extensively used as anticorrosive coatings on metals. A number of methods for the protection of metals against corrosion are recently focused on the possible use of metal oxide nanoparticles as either film forming corrosion inhibitors or in protective coatings [4]. This study describes the process of synthesizing and characterization of ZnO nanoparticles and then evaluating their anticorrosion performance using electrochemical studies were carried out in 0.1M HCl on mild steel.

II. EXPERIMENTAL

a) Materials: Zinc acetate (Zn (CH3COO)2•2H2O) and Oxalic acid (H2C2O4•2H2O) were purchased from HiMedia (AR) grade.

b) Methods:
FT-IR – spectrum is used to characterize the molecular structures of nanoparticles were performed on 4100 FT-Infrared spectrophotometer. The powder X-ray diffraction technique has been employed to identify the crystalline phases of the samples using Cu. Kα (1.5456Å). The surface morphology of the nanoparticles was recorded in JSM- 5610

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LV. SEM and EDAX analysis operating at 20 KV with different magnifications. Computer controlled CHI 650C workstation was used for all electrochemical studies. The electrochemical studies were carried out in a three electrode cell.

c). Synthesis of ZnO nanoparticles:

ZnO nanoparticles were synthesized by solution free mechanochemical reaction. Zinc acetate and oxalic acid were mixed in the ratio 1:3 by grinding in an agate pestle and mortar for 30 minutes at room temperature, forming the ZnC2O4.2H2O. Then ZnO nanoparticles were prepared by thermal decomposition of obtained ZnC2O4.2H2O at 500°C for 2 hrs. The chemical reaction of ZnO formation is written as following equation:

Zn (CH3COO) 2•2H2O + H2C2O4•2H2O → Zn (C2O4)•2H2O + 2CH3COOH + 2H2O
Zn(C2O4)•2H2O + ½ O2 → ZnO + 2CO2+ 2H2O

III. RESULT AND DISCUSSION

a) FT-IR Spectra:

Figure 1 shows the FT-IR spectrum of the ZnO nanoparticles synthesized by mechanochemical reaction method, which was acquired in the range of 400-4000 cm-1. The absorption bands at 538 and 486cm-1 which was shown the stretching vibration of Zn-O [5]. In addition, there is a weak adsorbed band at 1620 cm-1 is assigned O-H bending vibration.

b) X – Ray Diffraction Studies (XRD):

Figure 2 illustrates the X-ray diffraction pattern of the ZnO nanoparticles. The results revealed that the ZnO sample exhibit wurtzite structure [6] and the strongest three diffraction peaks at 2θ=23.68°, 24.80° and 37.65° which are in close agreement to JCPDS No.79-0208. The strong and sharp reflection peaks indicated that crystalline nature of the nanoparticles. The average crystallite size of the ZnO nanoparticles calculated using the Scherer's formula and value is 18nm.

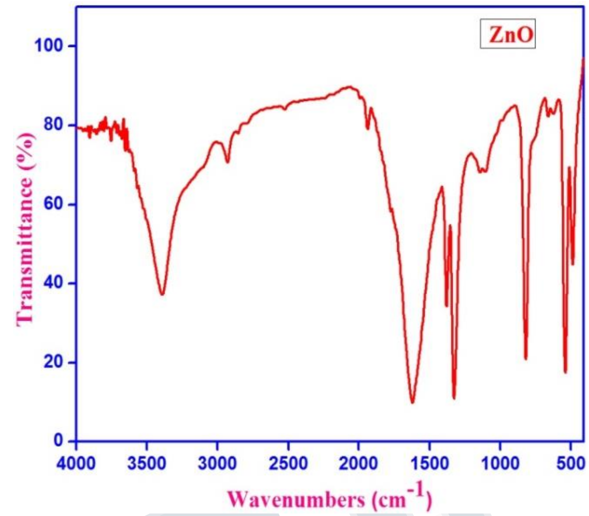

Fig 1: FT-IR spectrum of ZnO nanoparticles

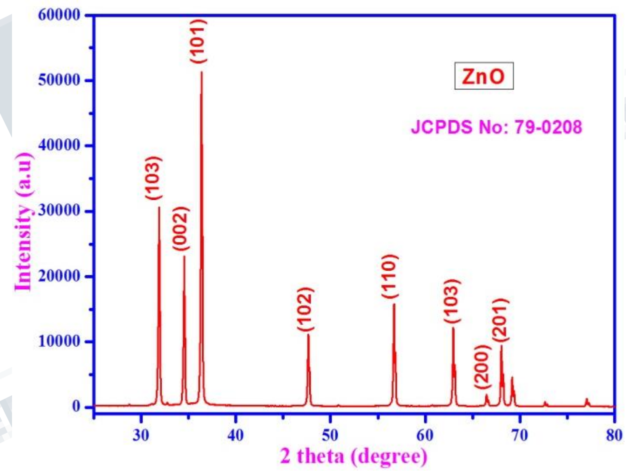

Fig 2: XRD spectrum of ZnO nanoparticles

c) Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray spectroscopy (EDS):

The SEM images of ZnO particles (Fig. 3), was observed that they are spherical shape and the particles are agglomerated. EDAX results showed that the composition of zinc and oxygen in ZnO nanoparticles is found to be 49.84 and 50.16%, respectively. No other peak related to any impurity has been detected in the EDS, which confirms that nanoparticles are composed only zinc with oxygen.

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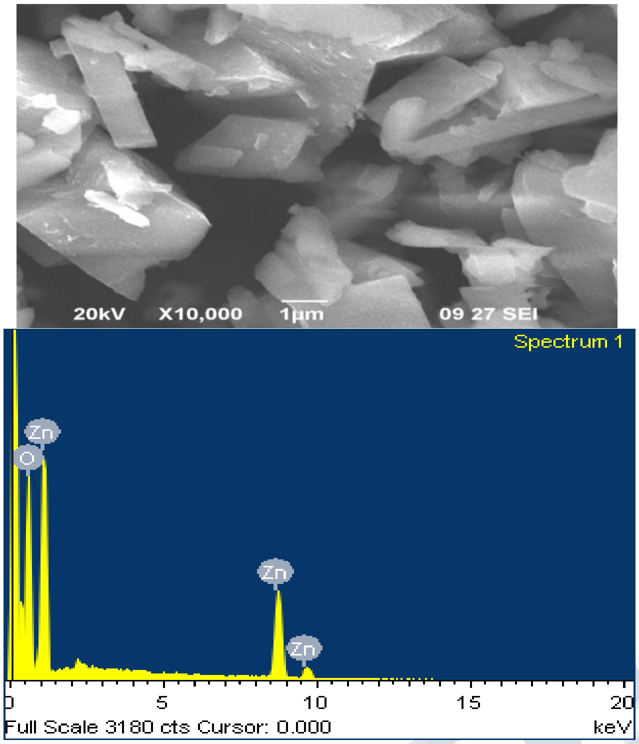


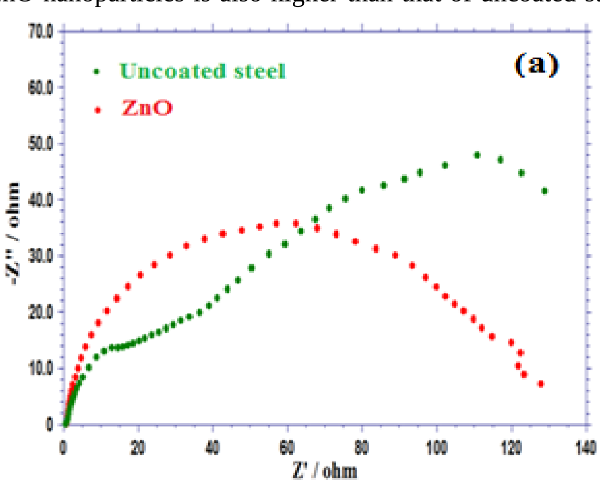
Figure 3 SEM image and EDS spectrum of ZnO nanoparticles

IV. ANTICORROSIVE PROPERTIES:

In the present study we have monitored the anticorrosion properties of coating on mild steel coupons by electrochemical impedance studies using ZnO nanoparticles in 0.1M HCl medium and 3.5% NaCl solution over 48 hrs.

a) Electrochemical Impedance Studies:

In the figures 4 shows the presence of a single semi circle shows the coating as a barrier. Electrochemical Impedance studies show the values of solution resistance (Rs), charge transfer resistance (Rct), double layer capacitance (Cdl), inhibition efficiency (%) and surface coverage (□) were determined via curve fitting of impedance. The inhibition efficiency of ZnO nanoparticles in the selected corrosive medium of 0.1M HCl and 3.5% NaCl solution are 73.98% and 81.83% respectively. The surface coverage value (□) of ZnO nanoparticles is also higher than that of uncoated steel samples.



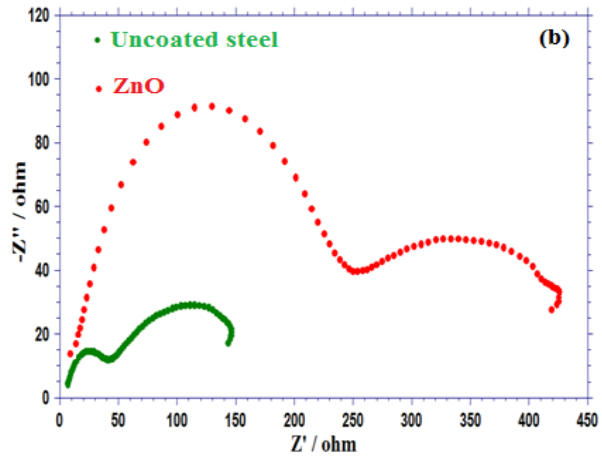
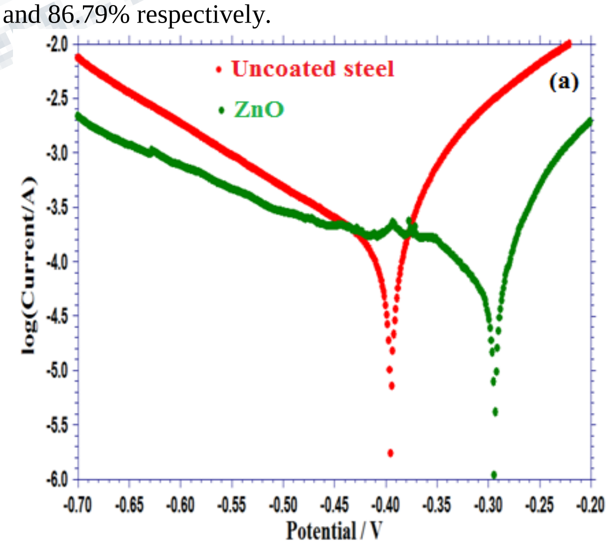


Figure 4 Nyquist plots in (a) 0.1M HCl and (b) 3.5% NaCl solution after immersion ZnO nanoparticles

b) Polarization Measurements:

The polarization measurements were carried out from cathodic potential and anodic potential with respect to the open circuit potential at a sweep rate of 50 mVs-1 to study the effect of inhibitor on mild steel corrosion. Polarization measurements show that the corrosion current values (Icorr) were found to be 0.1923 mA in 0.1M HCl and 0.1174 mA in 3.5% NaCl solution on mild steel samples. The inhibition efficiency of ZnO nanoparticles in the selected corrosive medium of 0.1M HCl and 3.5% NaCl solution are 68.59% and 86.79% respectively.



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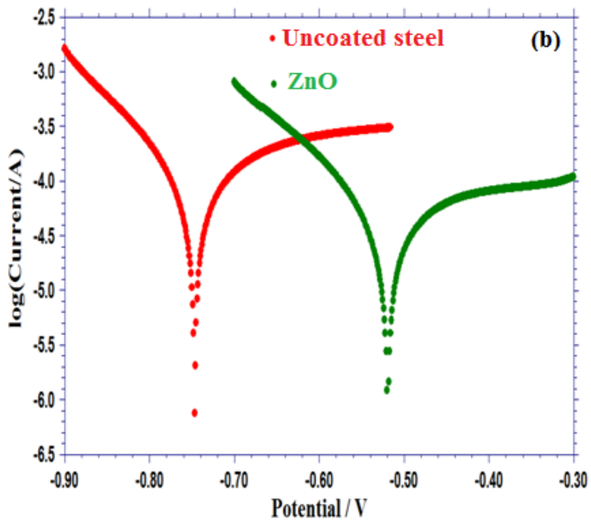

Figure 4 Tafel plots in (a) 0.1M HCl and (b) 3.5% NaCl solution after immersion ZnO nanoparticles

V. CONCLUSIONS

In the present study, the chemical reaction between Zn(CH3COO)2 and H2C2O4•2H2O continued forming of ZnO nanoparticles via mechanochemical reaction. The physico- chemical properties of the material were determined using FT-IR, XRD studies and SEM-EDAX studies. FT-IR spectra showed peaks in the region between 538 and 486cm-1 which corresponds to the stretching vibration of Zn – O band to confirm the formation of ZnO nanoparticles. From XRD studies and SEM-EDAX images, the ZnO nanoparticles can be considered as wurtzite structure. In electrochemical impedance result, it is clear that the protection efficiency for ZnO nanoparticles is higher than that of uncoated steel samples. Tafel curves shows that the protective action of the ZnO nanoparticles promotes a change of the corrosion potential. value. In the anticorrosion studies was conducted the electrochemically in the selected two corrosive medium (0.1M HCl and solution), ZnO nanoparticles acts as the poor anticorrosive behavior in 0.1M HCl medium. EIS and polarization studies agreed good anticorrosive behaviour of ZnO nanoparticles in 3.5% NaCl on mild steel samples.

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